# CALIBRATION OF THE INFRARED SPECTROMETER

by

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# INTRODUCTION

In general, a spectrometer is an instrument used for producing the spectrum of a given source of light. Ordinarily, the source of light is a narrow slit, and the spectrum is the collection of slit images of this source, there being one image for each wave length emitted by the light source.

Just as in the case when sunlight, under specific conditions, passes through water and produces a rainbow; so in a prism spectrometer, light passing through the prism is dispersed into its "rainbow" or spectrum, consisting of all the component wave lengths of the source light. Prisms of various materials may be used, some of the more common of which are glass, rock salt, lithium fluoride, and even liquids, such as water.

Prisms are able to produce spectra under particular conditions due to the dispersion phenomenon of certain media. Dispersion refers to the change in velocity in a medium when the wave length of the light is changed. This results in a deviation of a light beam which depends upon the wave length.

To present the electromagnetic theory of dispersion one must start with the assumption that in a dielectric material, since the electrons are more or less bound to their atoms, an applied electric field will only displace the electron until the restoring force is equal to the electric force. If the electric field is suddenly removed, the electron will perform a series of vibrations with a frequency which is the natural frequency of the electron and which depends upon the type of

atom. Of course in a given dielectric material there may be more than one natural frequency.

According to the electromagnetic theory, light consists of rapidly alternating electric and magnetic fields at right angles to each other and each at right angles to the direction of propagation. Therefore, when a beam of light traverses a dielectric material, the electron is subject to a force due to the electric field which alternates at the frequency of light. If this happens to be the natural frequency of vibration of the electron, a condition of resonance would result and maximum amplitude would be obtained. In this case almost all the energy of the disturbing field is absorbed, and that particular frequency of the incident light is not transmitted.

Another assumption must be made to the effect that there is a factor akin to friction involved whose magnitude is proportional to the velocity of the electron. With a large amplitude of vibration, large frictional losses are present. If, on the other hand, the frequency of the incident light is somewhat different from the natural frequency of the atom, the electron undergoes forced vibrations with much reduced amplitude, and the frictional losses are much smaller. Therefore, only part of the light energy is lost, and the dielectric is transparent for that wave length.

Full mathematical consideration of these ideas results in the development of an expression relating the velocity of the light in the dispersing medium and its wave length. The equation, simplified to apply to normal dispersion, is

$$\left(\frac{c}{v}\right)^2 = 1 + \frac{D\,\lambda^2}{\lambda^2 - \lambda_m^2}$$

where c is the velocity of light in a vacuum (and approximately that in air), v is the velocity in the medium under consideration, $\lambda$ is the wave length of the light, and $\lambda_m$ is the wave length corresponding to the natural frequency of the electron. D is a constant whose value depends on the charge on the electron, on its mass, on its natural frequency, and on the number of electrons in unit volume. Since the deviation depends upon the velocity, this expression then determines the deviation as a function of the wave length.

By definition, the ratio c/v is the index of refraction for the particular substance. In terms of n, the index of refraction, the above equation becomes

$$n^2 = 1 + \frac{D\,\lambda^2}{\lambda^2 - \lambda_m^2}$$

The graph of this equation is shown in Fig. 1.

From this graph it is seen that the index, and therefore the deviation of a light beam, depends on the wave length. Normal dispersion occurs in the region A-B of the curve, while the so-called anomalous dispersion occurs in the region such that $\lambda$ has values both greater and less than $\lambda_m$. Since dispersion depends upon the refractive index changing with the wave length, it is apparent from the graph that the greater the slope of the region being used, the greater is the dispersive power, and the slope is greatest near the absorption

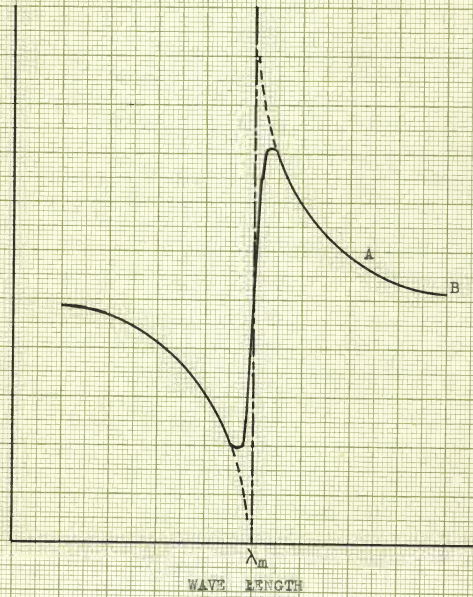


Fig. 1. Theoretical curve showing relationship between index and wavelength with absorption occuring at $\lambda_m$.

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band. All this is important in choosing a dispersing material for the region under investigation. For example, when working in the near infrared region, rock-salt prisms provide good dispersion from about 15 microns down to three or four. For wave lengths shorter than this, a lithium fluoride prism is desirable. For this region the dispersion of rock-salt is small and that of lithium fluoride is large since the latter has an absorption band near five microns.

## DESCRIPTION OF SPECTROMETER

The infrared spectrometer utilizes radiation of wave lengths longer than that of visible light. The one under consideration is a Perkin-Elmer spectrometer, Model 12A, equipped with a NaCl prism useful over a range of 2.5 to 15 microns. The instrument is shown in Plate I.

### Optical Path

The optical path, as viewed from above, is seen in Plate II, both in picture and diagram form. Continuous radiation from the globar source, G, is focused through the gas absorption cell, C, onto slit $S_i$ by means of the spherical mirror, $M_{ii}$. Light which passes through the entrance slit is brought into a parallel beam by the parabolic mirror, $M_{iii}$. It is then dispersed by the prism, reflected by the Littrow mirror, $M_{iv}$, dispersed again, and focused as a spectrum across the slit $S_{ii}$ by the parabolic mirror after reflection by the plane mirror, $M_v$. Only the rays of a narrow band of frequencies pass through the slit, $S_{ii}$ and they are focused on the upper junction of a compensated vacuum thermo-

couple by the spherical mirror, $M_{VII}$.

All focusing is done by front aluminized mirrors to eliminate, to the greatest possible degree, unwanted absorption and chromatic aberration, and so that the spectrometer may be focused with visible light. An opaque shutter, S, is situated at the exit port of the source housing.

## Source of Radiation

Continuous infrared radiation is supplied by a globar, G. It is a carborundum rod three-sixteenths inch in diameter and is electrically heated to 1000° C. The power supply, the housing of which is shown in Plate I, Fig. 3, furnishes five to six amperes at 40 to 50 volts to the globar through silver electrodes. The amount of power supplied to the globar is controlled so that over periods of several months, as the resistance of the globar varies with use, the temperature, and therefore the emission, can be kept constant. The entire globar is contained in a water jacket connected by rubber tubing to permanent plumbing.

## Absorption Cell

The gas absorption cell was constructed by sealing a section of glass tubing five cm in diameter and ten cm long at both ends with parallel-faced rock-salt plates. The light beam is passed through the cell longitudinally so that it has an absorption path of ten cm and does not pass through any glass, only rock-salt. A small tube with stop cock leading off from the side of the cell provides a means of adding or

## EXPLANATION OF PLATE I

Fig. 2. Front view of spectrometer.

Fig. 3. View of associated apparatus.

PLATE I

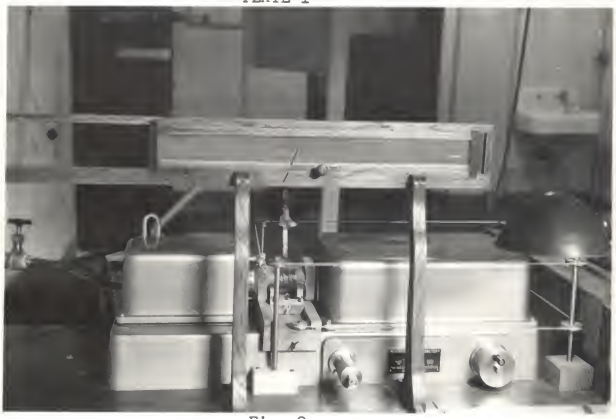


Fig. 2.

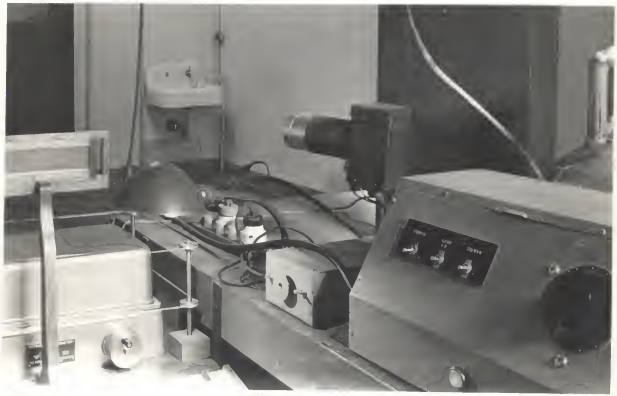
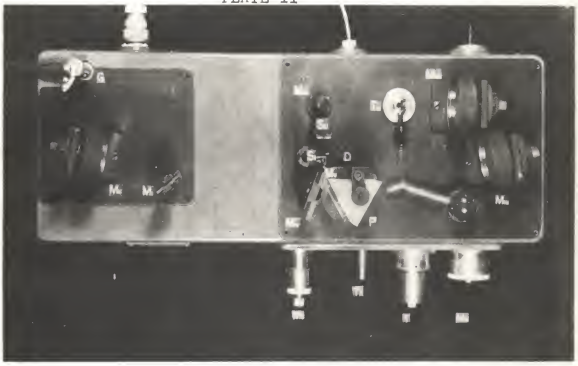


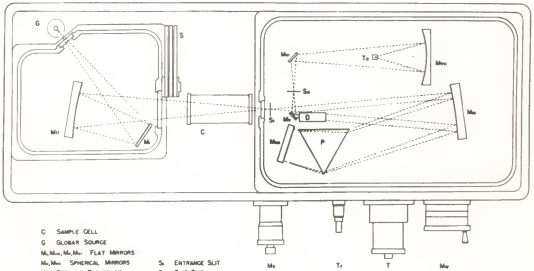
Fig. 3.

EXPLANATION OF PLATE II

Plan view with the covers off and plan diagram of the spectrometer.

PLATE II




C Sample Cell
G Globar Source
$M_i, M_{i'}, M_c, M_{c'}$ Flat Mirrors
$M_c, M_{c'}$ Spherical Mirrors
$M_w, M_{w'}$ Off axis Paraboloid
$M_s$ Slit Micrometer
$M_w$ Wavelength Micrometer
P Prism
S Shutters
$S_s$ Entrance Slit
$S_e$ Exit Slit
T Turret Drum
$T_r$ Turret Release
$T_e$ Thermocouple
D Temperature Compensator

Perkin-Elmer Infrared Spectrometer
Model 12A

changing samples. The cell may be seen in place in Fig. 2.

### Slits

The entrance and exit slits, $S_i$ and $S_{ii}$, are controlled simultaneously by the slit micrometer, $M_s$. It reads directly in thousandths of millimeters from zero to two mm.

### Wave length Micrometer

The wave length or frequency setting is controlled by the wave length micrometer, $M_w$, which rotates the mirror, $M_{iv}$, thus allowing a different section of the spectrum to fall on the exit slit. The drum calibration is arbitrary.

### Thermocouple

The thermocouple, $T_c$, is a high vacuum, compensated type with the following properties:

| | |
|---|---|
| Junction | Bismuth-bismuth tin |
| Total resistance | 12 ohms |
| Area of target | .6 x 4 mm. |
| Window | KBr |
| Approximate response time | 1 second |
| Sensitivity | .3 microvolts/erg/second |
| Compensation | 95+% |

The thermocouple housing is first evacuated by a mechanical pump, and this vacuum is increased by a carbon getter bulb which extends down under the table on which the spectrometer rests. During operation of the spectrometer, this bulb is

kept immersed in liquid air to enable it to absorb more air.

## Galvanometer

The output of the thermocouple is measured by a high sensitivity Leeds and Northrup galvanometer, type 2284-x, with the following characteristics:

| | |
|---|---|
| Sensitivity | 0.048 V/mm. |
| Damping resistance | 9 ohms |
| Period | 6.2 seconds |
| Resistance | 15 ohms |

The galvanometer is supported on a Muller (7) suspension inside a specially constructed box, part of which may be seen in Plate I, Fig. 3. A small window on the front of the box permits entrance of a light beam which is reflected by the galvanometer mirror out of the box and a distance of about 12 feet where it is again reflected about 12 feet where it finally impinges on a ground glass metric scale, which appears in Plate I, Fig. 2. The total optical path is thus about 24 feet.

Ordinarily, the galvanometer drifts so much that the scale must be reset on zero after every reading, so the scale is held in a sliding frame. To provide a greater range of control, a potentiometer was constructed and connected in parallel with the thermocouple. It is energized by two 1.5 volt dry cells and is contained in a small box shown in the center of Plate I, Fig. 3.

## OPERATION

The spectrometer was used only in obtaining absorption spectra. In operation, the shutter, S, is opened allowing the light beam from the globar source to fall on the absorption cell. The transmitted light is dispersed as described above. The frequency or wave length of light which passes through the exit slit is chosen by the wave length micrometer, $M_w$. The galvanometer deflects in proportion to the intensity of the radiation falling on the thermocouple.

## CALIBRATION CURVE

Since the scale on the wave length micrometer is an arbitrary one, the first thing that must be done after the spectrometer is put into operation, is to calibrate the instrument. That is, determine the frequency for a given micrometer setting. Theoretically, it would be possible to use the equation given above for this determination, but it would involve finding the refractive index of the prism as a function of the angles of incidence and refraction and the value of these angles in terms of micrometer settings. It is easier to construct a calibration curve from experimental data.

This is carried out by determining the positions of absorption bands of several common substances. Since $H_2O$ vapor and $CO_2$ occur in the atmosphere in appreciable amounts, no sample cell was needed to obtain their spectra. A graph of the data obtained is shown in Plate III with wave length micrometer

settings plotted as abscissas and galvanometer deflections in cm as ordinates. This put the data in a form so that enough detail was shown to permit each band to be recognized by its fine structure. Then, by referring to absorption spectra given in (5), particular wave lengths were assigned to the absorption dips, only some of which are shown on the graphs.

This was also done for $NH_3$ gas, but it necessitated the use of the gas absorption cell described above. Also, it was necessary to construct an ammonia generator. Ammonium chloride and sodium hydroxide were placed in an evacuated container with a little water. The chemical equations for the reaction are

$$NH_4Cl + NaOH \longrightarrow NaCl + NH_4OH$$
$$NH_4OH \longrightarrow NH_3 + H_2O.$$

The ammonia gas was led through a drying tube of sodium hydroxide and then to the absorption cell. The pressure of the gas was determined by a closed-tube, mercury manometer.

The spectra of these three gases provided calibration points over a range extending from the lowest point on the $NH_3$ spectra, numbered 723.5 $cm^{-1}$ to the highest $CO_2$ absorption point at 3882 $cm^{-1}$. The calibration curve was plotted with the frequencies as abscissas and their corresponding micrometer settings as ordinates. The curve connecting these points was smoothed according to a method similar to one given by Worthing and Geffner (9). Since the curve was practically a straight line below 800 $cm^{-1}$, it was considered justifiable to extrapolate the curve from a micrometer setting of about 800 down to

EXPLANATION OF PLATE III

Graphs plotted from experimental data with frequencies in $cm^{-1}$ assigned to absorption dips.

PLATE III
DEFLECTION
GALVANOMETER
MICROMETER SETTING
$H_2O$ IN AIR
$CO_2$ & $H_2O$ IN AIR
$NH_3$
1830
1774
1736
1671
1618
1542
1459
1420
2387
3817
3741
3662
1143
1117.4
1075.8
1054.4
1033.8
1012.8
992.8
972.7
948.8
924.3
908.4
883
854
848
830.9
812.4
807.7
798.3
792
788.4
776.8
771.1
753.7
745.3
738.2
732.5
723.5
1700
1750
1800
1850
1900
1950
2000
1100
1200
1300
1400
1500
900
1000
800

The final calibration curve is shown in Plate IV.

## USE OF CALIBRATION CURVE

As an example of one way in which the spectrometer and calibration curve may be used, a spectrum was run using fuel gas drawn from the city mains as a sample. Galvanometer deflections were obtained for wave length micrometer settings from 900 to 1800. This data was checked once, and in some regions two times. Then, from the calibration curve, the corresponding wave lengths were picked off for each micrometer setting. This gave data showing galvanometer deflection versus wave length. But since part of the light path in the spectrometer is through the atmosphere, any absorption band, which shows up in this data by a low galvanometer deflection, may be due partially or wholly to substances in the atmosphere. Therefore, for each micrometer setting, a galvanometer deflection was obtained with the fuel gas sample in the light path and one with the gas cell out of the path. The former reading divided by the latter times 100 gave the percent transmission of the gas sample for that wave length. Percent transmission subtracted from 100 gave the percent absorption. The data in this form was plotted, as shown in solid lines in Plate V.

In this form the absorption bands can be compared with characteristic bands of published spectra (3,4). The comparison that was made is shown in Table 1 and Plate V.

EXPLANATION OF PLATE IV

Calibration Curve.

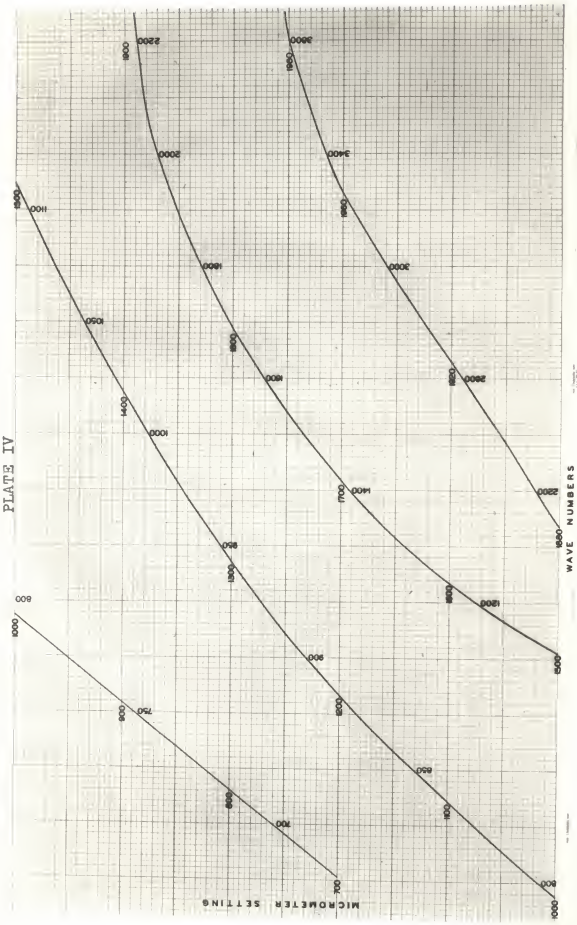



PLATE IV

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Table 1. Identification of observed absorption bands.

| Observed frequency | Compound producing band | Frequency from pure compound |
|---|---|---|
| 822 | $C_2H_6$ | 812 |
| 829 | $C_2H_6$ | 820 |
| 836 | $C_2H_6$ | 832 |
| 845 | $C_2H_6$ | 835 |
| 930 | unidentified | |
| 965 | unidentified | |
| 990 | unidentified | |
| 1012 | unidentified | |
| 1036 | $C_3H_8$ | 1040 |
| 1047 | $C_3H_8$ | 1054 |
| 1066 | $C_3H_8$ | 1070 |
| 1076 | unidentified | |
| 1104 | unidentified | |
| 1190 | $CH_4$ | 1189 |
| 1220 | $CH_4$ | 1220 |
| 1242 | $CH_4$ | 1245 |
| 1255 | $CH_4$ | 1260 |
| 1264 | $CH_4$ | 1266 |
| 1295 | $CH_4$ | 1303 |
| 1337 | $CH_4$ | 1350 |
| 1348 | $CH_4$ | 1350 |
| 1415 | $C_2H_6$ | 1404 |
| 1435 | $C_2H_6$ | 1500 |
| 1459 | $C_2H_6$ | 1500 |
| 1486 | $C_2H_6$ | 1500 |
| 1501 | $C_2H_6$ | 1500 |
| 1516 | $C_2H_6$ | 1500 |
| 1531 | $C_2H_6$ | 1500 |
| 1546 | $C_2H_6$ | 1500 |
| 1561 | $C_2H_6$ | 1500 |
| 2326 | $CO_2$ | 2327 |
| 2365 | $CO_2$ | 2369 |
| 2860 | $CH_4$ | 2820 |
| 2942 | $CH_4$ | 2960 |
| 3035 | $CH_4$ | 3028 |
| 3100 | $CH_4$ | 3120 |

It is noted that several of the observed absorption bands between 1400 and 1600 $cm^{-1}$ have been identified with the one broad ethane band. This is possible because the ethane band came from a spectrum of low resolution. The unidentified

EXPLANATION OF PLATE V

Absorption spectra of commercial fuel gas. Solid curve is the result of this investigation. Dashed curves, from reference (4), are due to the pure substances as follows:

A-A' ethane

B-B' methane

C-C' ethane

D-D' carbon dioxide

E-E' methane

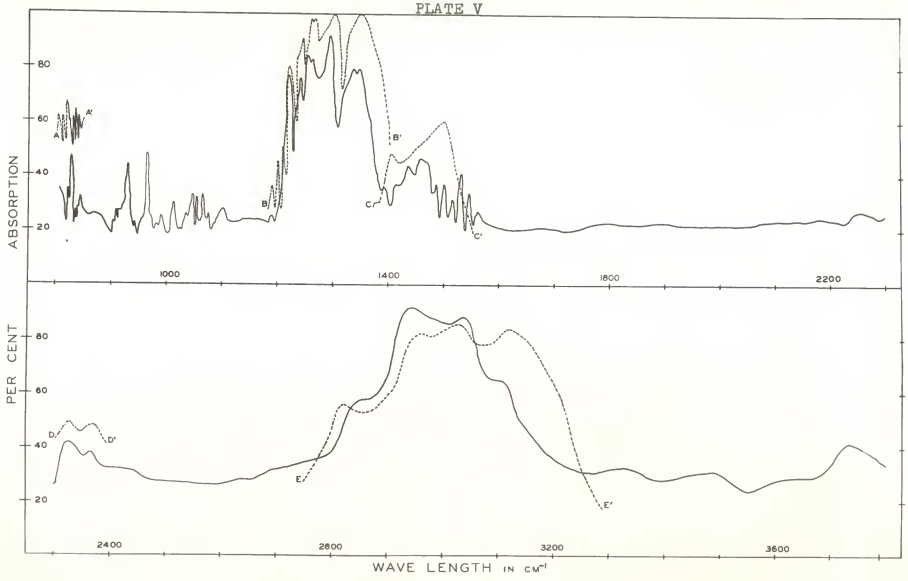
PLATE V
ABSORPTION
80
60
40
20
A
A'
B
B'
C
C'
1000
1400
1800
2200
PER CENT
80
60
40
20
D
D'
E
E'
2400
2800
3200
3600
WAVE LENGTH IN CM⁻¹

bands are quite probably due to other hydrocarbons and water vapor.

As a check on these findings, an analysis of the fuel gas was obtained from the gas company.[1] This analysis is shown in Table 2.

Table 2. Chemical analysis[1] of Manhattan, Kansas, city fuel gas on January 28, 1948.

| Component | Percent |
|---|---|
| Carbon dioxide | 0.24 |
| Oxygen | 0.00 |
| Methane | 83.60 |
| Ethane | 10.71 |
| Residual | 5.45 |

[1]Obtained from the office of the Kansas Power and Light Company, Manhattan, Kansas.

ACKNOWLEDGMENT

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